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Evidence of continuous evolution of smectic A_2 from smectic A_d

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We present here precise measurements of the layer spacing for two compounds, viz. 4-*n*-heptyloxyphenyl-4′-(4″-cyanobenzoyloxy)benzoate and 4-*n*-undecyloxyphenyl-4′-(4″-cyanobenzyloxy)benzoate. Contrary to earlier reports our data do not show any jump in the layer spacing at the expected A_d–A_2 transition temperature, showing thereby that for both compounds A_2 evolves continuously from the A_d phase.

It is well known that tri-aromatic ring compounds with a terminal cyano or nitro group exhibit different polymorphic forms of the smectic A phase [1]. These phases, which have been classified [2] on the basis of X-ray diffraction patterns exhibited by monodomain samples, are: monolayer (A_1), partially bilayer (A_d), bilayer (A_2) and the recently observed [3] incommensurate (A_{ic}) phases. In addition, two types of antiphases ($\tilde{A}$ and A_{cr}) with different symmetries are also known [4]. However, it is now generally believed [5] that these antiphases are not uniaxial and hence cannot be classified as A phases.

Transitions between different A phases have been observed. For the most part, however, these A–A transitions have been seen only in binary systems. The only A–A transition that is exhibited by a single component system appears to be the A_d–A_2 transition [6]. This transition is, by symmetry arguments [7], expected to be first order which could end as a critical point of the gas–liquid kind.

There have been experimental attempts [8, 9] (using differential thermal analysis and X-ray diffraction techniques) to investigate whether such an A_d–A_2 critical point exists in a temperature–molecular length phase diagram. These experiments were conducted on two homologous series, viz. 4-*n*-alkoxyphenyl-4′-(4″-cyanobenzoyloxy)benzoates (DB*n*OCN) and 4-*n*-alkoxyphenyl-4′-(4″-cyanobenzyloxy)benzoates (*n*OPCBOB). In both cases the layer spacing, *d*, showed a marked jump at the A_d–A_2 transition for the lowest homologue (viz. DB7OCN and 11OPCBOB) and the magnitude of this jump decreased with increasing chain length. For large chain lengths, instead of an abrupt jump in *d*, only a change of slope was observed in the *d* versus temperature plots. Two alternative explanations were given for this result [9]. There might exist in the temperature–molecular length diagram a tricritical point on the

A_d–A_2 line or the A_d–A_2 transition boundary might end as a critical point. Since it is now believed from theoretical considerations [7] that the A_d–A_2 transition cannot be second order, the latter explanation seems more likely. As a first step to locate the A_d–A_2 critical point, we have carried out very precise measurements of *d* as a function of temperature in DB7OCN and 11OPCBOB.

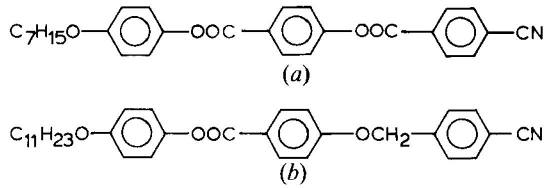

Figure 1. Molecular structure of (*a*) DB7OCN and (*b*) 11OPCBOB.

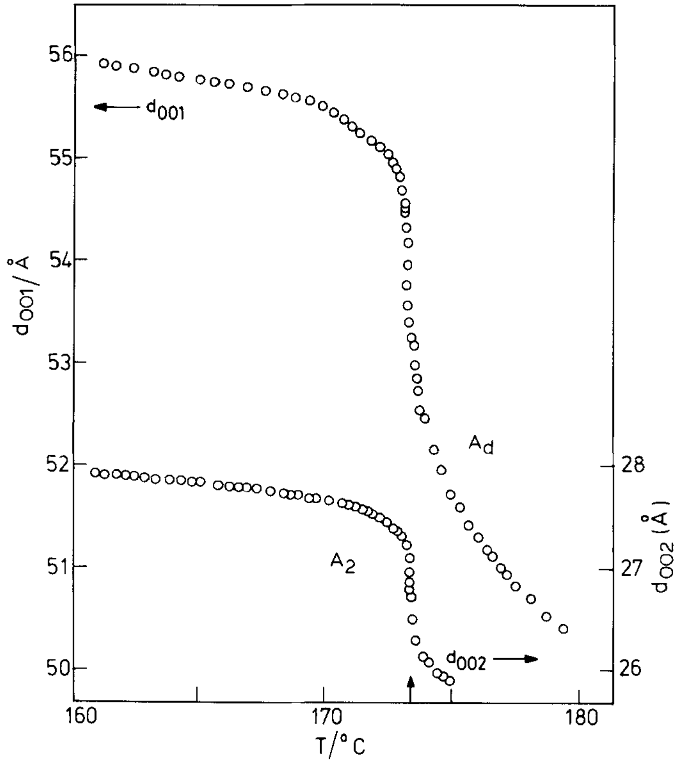

Figure 2. Temperature variation of the layer spacing corresponding to the (001) and (002) reflections in the A_d and A_2 phases of DB7OCN. The vertical arrow in this figure as well as in figures 3–5 indicates the temperature at which the A_d–A_2 transition is expected from D.S.C. runs.

The compounds used in the present study were synthesized by us. (Their molecular structures are shown in figure 1.) D.S.C. runs showed large peaks at temperatures which agree well with the reported A_d–A_2 transition temperatures. The X-ray diffraction experiments were conducted using a computer-controlled Guinier diffractometer (Huber 644). By means of a bent quartz monochromator used in the Johansson geometry, Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ lines were separated and only the $K_{\alpha 1}$ line was used for the experiment. The liquid-crystalline samples in a Lindemann capillary (0·5 mm diameter)

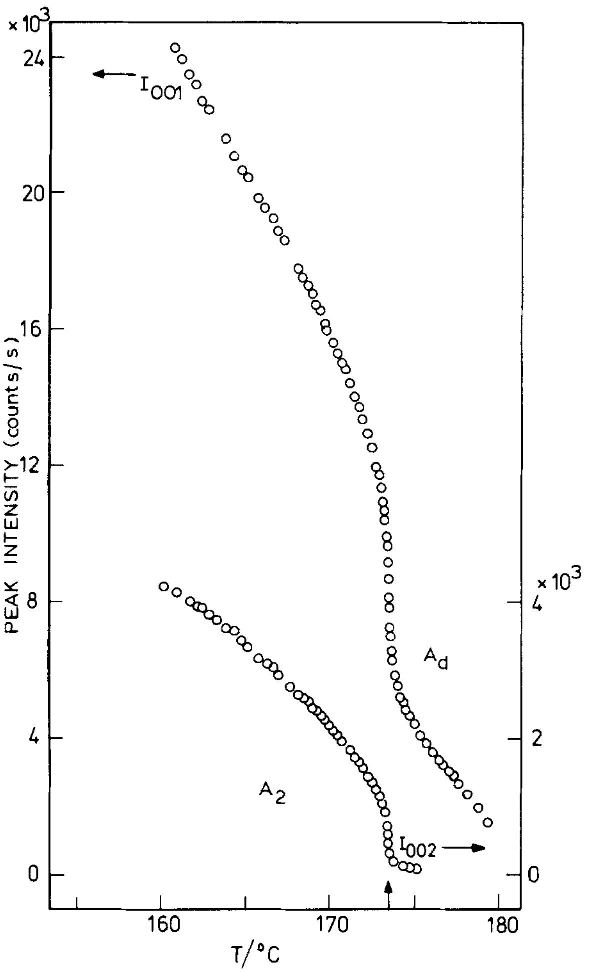

Figure 3. Temperature variation of the intensity of the 001 and 002 diffraction peaks in the A_d and A_2 phases of DB7OCN.

were oriented by slow cooling from the nematic phase in the presence of a magnetic field. The detector (NaI scintillation counter, Bicron) was mounted on a rotatable graduated base whose angular scans could be controlled by a stepping motor. A Hewlett-Packard computer (HP-86B) served to control the angular movement of the detector as well as providing data acquisition and analysis.

A typical experiment was carried out in the following manner. An initial scan was taken (along the equatorial plane) by changing the position of the counter in steps of 0·01° and the approximate θ position of the diffraction peak was obtained. A refined θ scan was then taken around this θ position by moving the counter in steps of 0·001°. The data were fitted to a second degree polynomial by using a least-squares-fit program. The value of θ obtained in this manner was used in the calculation of the layer spacing. The on-line θ refinement at any temperature required about 5 min. During this period the temperature of the sample was maintained to a constancy of ± 10 mK. The precision in the layer spacing measurement is estimated to be ±0·05 Å or better.

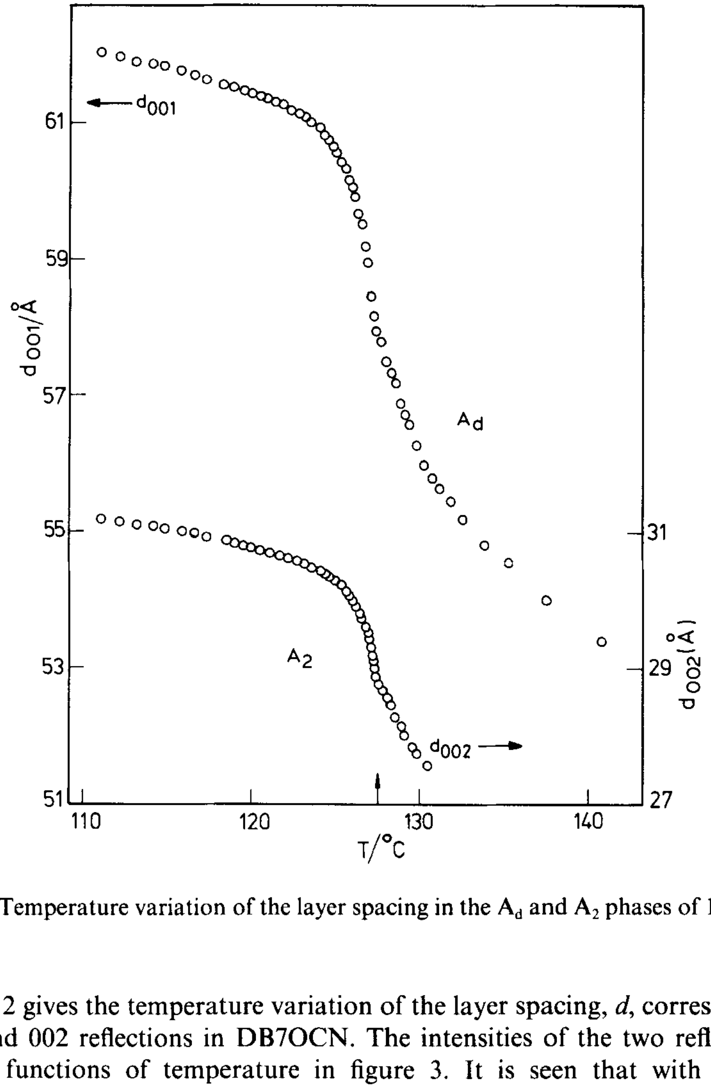

Figure 4. Temperature variation of the layer spacing in the A_d and A_2 phases of 11OPCBOB.

Figure 2 gives the temperature variation of the layer spacing, *d*, corresponding to the 001 and 002 reflections in DB7OCN. The intensities of the two reflections are shown as functions of temperature in figure 3. It is seen that with decreasing temperature the layer spacing for the 001 reflection, i.e. d_{001}, shows a steep increase on approaching the A_2 phase. It should also be mentioned that the second harmonic, i.e. the (002) reflection, appears as a faint peak in the A_d phase itself well before the expected A_d–A_2 transition temperature and grows in strength with decreasing temperature. The exact temperature of its appearance depends essentially on experimental conditions. At all temperatures the 002 peak is exactly at twice the wave vector of the 001 peak. In order to observe a possible jump in the layer spacing at the A_d–A_2 transition, we collected data at close intervals of temperature (75–100 mK) on either side of the expected transition temperature, the precision in the determination of *d* being 0·05 Å (as mentioned earlier) at every temperature. Our data obtained with this precision does not show any jump in the layer spacing; in fact both d_{001} and d_{002} vary smoothly right through the temperature at which the A_d–A_2 transition is expected from D.S.C. results. The intensities of the two reflections also show a continuous variation (figure 3). Essentially similar results have also been obtained for 11OPCBOB (figures 4 and 5).

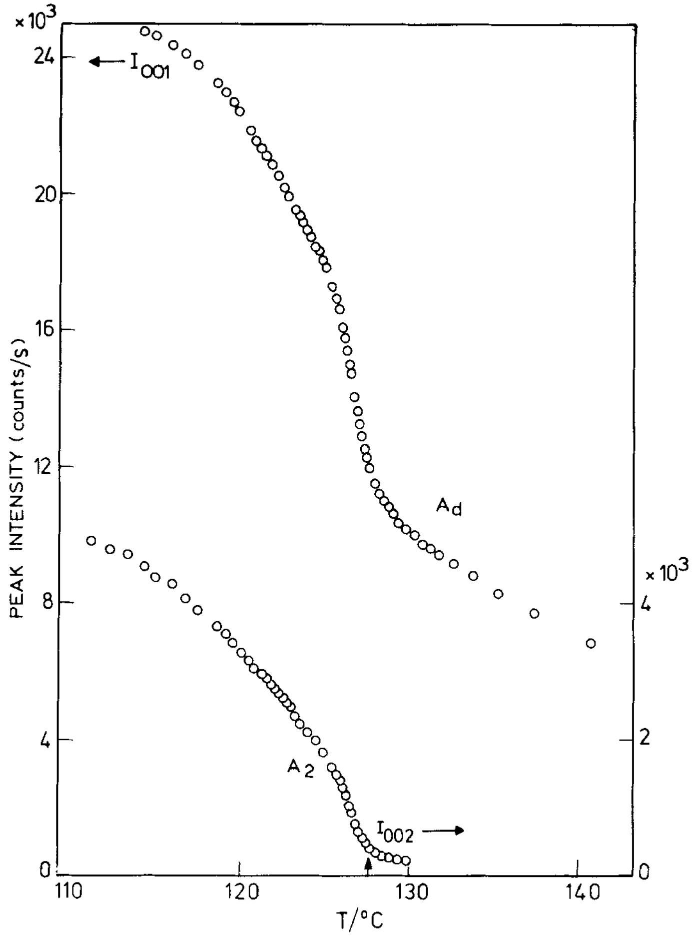

Figure 5. Temperature variation of the intensity of the diffraction peaks in the A_d and A_2 phases of 11OPCBOB.

As mentioned earlier, X-ray studies [8, 9] on the very same substances appeared to show pronounced jumps in the layer spacing (about 4·9 Å for DB7OCN and about 4·3 Å for 11OPCBOB) at the A_d–A_2 transition. However, we believe that these jumps are experimental artefacts since there are no measurements in the vicinity of the transition. In fact our data, which are of higher precision and which have been collected in the close proximity of the expected A_d–A_2 transition temperature, definitely do not show any evidence of a jump in layer spacing, there being only a point of inflection at the temperature at which the D.S.C. run shows a peak. Hence the A_d–A_2 transition does not appear to be first order in either of the two compounds. Theoretical arguments based on symmetry considerations rule out a second order transition. We therefore believe that our results imply a *continuous evolution of the A_2 phase from the A_d phase without a phase transition.* Recent high resolution a.c. calorimetric results on DB7OCN also seem to lead to the same conclusion [10].

Thus we infer that both DB7OCN and 11OPCBOB do not really exhibit the A_d–A_2 transition at all, but they lie above but close to an A_d–A_2 critical point in the temperature–molecular length diagram. Further studies on other systems for which the A_d–A_2 transition has been reported in the literature are in progress in order to find a possible A_d–A_2 critical point.

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